



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

:

Francois COURT et al.

Group Art Unit: 1772

Serial No.: 09/762,677

:

Examiner: AUGHENBAUGH, W.

Filed: 4/5/01

:

For: TUBE FOR GASOLINE TRANSPORT

DECLARATION UNDER 37 C.F.R. §1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Dr. Yves Gnanou, being duly warned hereby state the following:

I am an expert in the polymerization arts, having considerable experience in the area. I am currently Director of Research-CNRS and Head of the Laboratory of Chemistry and Organic Polymers at the University of Bordeaux. I am also currently Adjunct Professor in the Department of Chemistry at the University of Florida. My CV is attached.

I have studied the disclosure of USP 4,423,188 (Witschard), and it is clear that patentees do not disclose linear triblock polymers, nor a process for their production, in which polymers a first block is incompatible with fluoro-resin, a second block is incompatible with fluoro-resin and the first block, and a third block is incompatible with fluoro-resin and the first two blocks.

In anionic polymerization the synthesis of block copolymers obeys certain rules that are very strict:

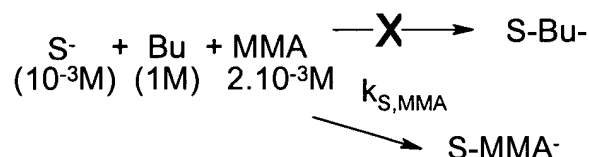
1. Monomers are to be polymerized in a particular order that depends on their position in the ladder of electrophilicity; the least electrophilic ones must be polymerized first and the rest in the increasing order of their *electroaffinity*. For example, in the case

of poly(styrene-b-butadiene-methyl methacrylate), styrene must be polymerized first, then butadiene and finally methyl methacrylate.

2. Unless closely positioned in the ladder of electroaffinity, monomers cannot undergo a real anionic copolymerization like in regular radical copolymerization, but only sequential polymerization. For instance, should styrene and methyl methacrylate be added at once in a medium containing BuLi(initiator), only the second monomer will be polymerized - due to its higher electroaffinity, styrene remaining unconverted.

In the preparation of a styrene-butadiene block polymer, after the growth of the first polystyrene block (S^-) by anionic means, butadiene is the second monomer to be introduced/polymerized; it has to be absolutely free of any residues or vinyl pyridine, acrylonitrile, alkylesters of acrylic acid, all monomers characterized by a much higher electroaffinity than butadiene and thus unable to anionically copolymerize with butadiene.

Let us take an example with $10^{-3}M$ of "living" polystyrene carbanionic chains (S^-) being prepared in a separate vessel to which is added 1M of butadiene (Bu) containing $2 \cdot 10^{-3}M$ of impurities in the form of residues of either vinyl pyridine (VP), acrylonitrile (AN), or alkyl (meth)acrylate (MMA):



$k_{S,Bu}$ being very small compared to $k_{S,MMA}$, S^- will exclusively react with MMA and only $S-MMA^-$ will be eventually formed, Bu being left untouched. On the other hand, $S-MMA^-$ once formed cannot react with Bu ($k_{MMA,Bu} = 0$) for the reasons mentioned above. This example shows how essential it is to get rid of any polar monomers of higher electroaffinity than Bu at the time of adding the latter. In the patent of Witschard, it is claimed (in col. 8, lines 32 - 44) that "if desired, the alkadiene added can contain ... minor proportions ... of residues of VP, An, MMA" which is totally wrong.

Should the concentration of these residues be comparable to that of growing anions $[S^-]$, the latter will exclusively react with these residues and not with the alkadiene. If the concentration of these residues is lower than that of $[S^-]$, then an equivalent concentration of copolymer chains will not contain any alkadiene. As a result, Witschard does not disclose the preparation of a triblock polymer containing MMA.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date

Yves Gnanou

Living Polymerization Methods

OWEN W. WEBSTER

Living polymerization techniques can be used to achieve a high degree of control over polymer chain architecture. Examples of the type of polymers that can be synthesized include block copolymers, comb-shaped polymers, multi-armed polymers, ladder polymers, and cyclic polymers. This control of structure, in turn, results in polymers with widely diverse physical properties, even though they are made from readily available low-cost monomers.

SYNTHETIC POLYMERS ARE LONG-CHAIN MOLECULES POSSESSING uniform repeat units (mers). The chains are not all the same length. These giant molecules are of interest because of their physical properties, in contrast to low molecular weight molecules, which are of interest due to their chemical properties. Possibly the most useful physical property of polymers is their low density versus strength. Dramatic uses of this property are demonstrated by the nonstop circumnavigation of the world by a "plastic" airplane on one tank of gas and by the construction of an airplane light enough to fly more than 110 km nonstop under human pedal power.

When synthetic polymers were first introduced, they were made by free radical initiation of single vinyl monomers or by chemical condensation of small difunctional molecules. The range of their properties was understandably meager. Random copolymers next entered the picture, greatly expanding the range of useful physical properties such as toughness, hardness, elasticity, compressibility, and strength. However, polymer chemists realized that their materials could not compare with the properties of natural polymers, such as wool, silk, cotton, rubber, tendons, and spider webbing. The natural polymers are generally condensation polymers made by addition of monomer units one at a time to the ends of growing polymer chains. Polymerization of all chains stops at identical molecular weights. For some time polymer chemists have realized that to approach nature's degree of sophistication, new synthetic techniques would be needed.

Conventional chain-growth polymerizations, for example, free radical synthesis, consist of four elementary steps: initiation, propagation, chain transfer, and termination. As early as 1936, Ziegler (1) proposed that anionic polymerization of styrene and butadiene by consecutive addition of monomer to an alkyl lithium initiator occurred without chain transfer or termination. During transferless polymerization, the number of polymer molecules remains constant. Since there is no termination, active anionic chain ends remain after all of the monomer has been polymerized. When fresh monomer is added, polymerization resumes. The name "living polymerization"

was coined for the method by Szwarc (2) because the chain ends remain active until killed. (The term has nothing to do with living in the biological sense.) Before Szwarc's classic work, Flory (3) had described the properties associated with living polymerization of ethylene oxide initiated with alkoxides. Flory noted that since all of the chain ends grow at the same rate, the molecular weight is determined by the amount of initiator used versus monomer (Eq. 1).

$$\text{Degree of polymerization} = [\text{monomer}]/[\text{initiator}] \quad (1)$$

Another property of polymers produced by living polymerization is the very narrow molecular weight distribution (3). The polydispersity (D) has a Poisson distribution, $D = \bar{M}_w/\bar{M}_n = 1 + (1/dp)$; \bar{M}_w is the average molecular weight determined by light scattering, \bar{M}_n is the average molecular weight determined by osmometry, and dp is the degree of polymerization (the number of monomer units per chain). The values of \bar{M}_w and \bar{M}_n can also be determined by gel permeation chromatography (GPC). A living polymerization can be distinguished from free radical polymerization or from a condensation polymerization by plotting the molecular weight of the polymer versus conversion. In a living polymerization, the molecular weight is directly proportional to conversion (Fig. 1, line A). In a free radical or other nonliving polymerization, high molecular weight polymer is formed in the initial stages (Fig. 1, line B), and in a condensation polymerization, high molecular weight polymer is formed only as the conversion approaches 100% (Fig. 1, line C).

Some General Features of Living Polymerizations

Living polymerization techniques give the synthetic chemist two particularly powerful tools for polymer chain design: the synthesis of block copolymers by sequential addition of monomers and the synthesis of functional-ended polymers by selective termination of living ends with appropriate reagents. The main architectural features available starting with these two basic themes are listed in Table 1 along with applications for the various polymer types. Although living polymerization of only a few monomers is nearly perfect, a large number of other systems fit theory close enough to be useful for synthesis of the wide variety of different polymer chain structures shown in Table 1. In general, the well-behaved living systems need only an initiator and monomer, as occurs in the anionic polymerization of styrene, dienes, and ethylene oxide. For an increasing number of monomers, more complex processes are needed to retard chain transfer and termination. These systems use initiators, catalysts, and sometimes chain-end stabilizers. The initiator begins chain growth and in all systems is attached (or part of it, at least) to the nongrowing chain end. The catalyst is necessary for initiation and propagation but is not consumed. The chain-end sta-

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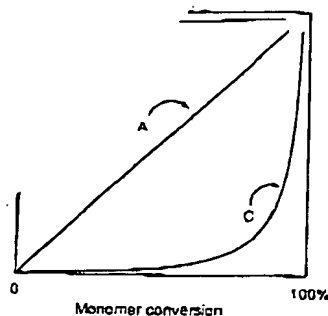


Fig. 1. Molecular weight conversion curves for various kinds of polymerization methods: (A) living polymerization; (B) free-radical polymerization; and (C) condensation polymerization.

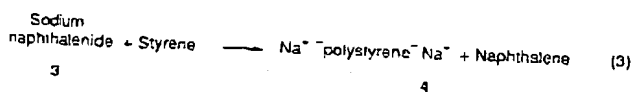
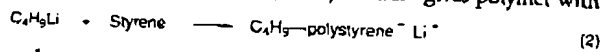
bilizer usually decreases the polymerization rate. When the catalyst is a Lewis acid (electron-pair acceptor), the stabilizer will likely be a Lewis base (electron-pair donor), and vice versa. In all systems, the initiation step must be faster than or the same rate as chain propagation to obtain molecular weight control. If the initiation rate is slower than the propagation rate, the first chains formed will be longer than the last chains formed. If an initiator with a structure similar to that of the growing chain is chosen, the initiation rate is assured of being comparable to the propagation rate. A number of living systems operate better if excess monomer is present. A possible explanation is that the living end is stabilized by complexation with monomer (4). Large counterions tend to be more effective than small counterions in living polymerization systems even when the ionic center is only indirectly involved.

Anionic, cationic, covalent, and free radical processes for living polymerization are described below along with applicable monomers. The best conditions for polymerization of individual monomers are also described. Although many mechanistic questions have not been resolved, the most probable pathways for chain growth are given. Applications that appear to have high potential are pointed out.

Anionic Living Polymerizations

The major monomer classes that yield to anionic living polymerization techniques are styrenes, butadienes, methacrylates, acrylates, ethylene oxide, hexamethylcyclotrisiloxane, and lactones.

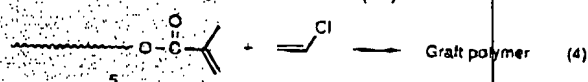
Styrene and substituted styrenes with non-base-sensitive groups have been the most studied monomers for living polymerization (5). Butyl lithium, 1, and sodium naphthalenide (2), 3, are examples of excellent initiators (Eqs. 2 and 3). Butyl lithium gives polymer with



one reactive end, 2, and sodium naphthalenide gives polymer with two reactive ends, 4. The use of 2 and 4 as initiators for other monomers results in AB (Table 1, no. 3) and ABA (Table 1, no. 4) block polymers. Treatment of 2 or 4 with ethylene oxide provides hydroxy-ended polymers (6) (Table 1, nos. 1 and 2).

A macromonomer, 5, results from treatment of hydroxy-ended polymer with methacryl chloride (7). Copolymerization of 5 with another monomer such as vinyl chloride gives a graft polymer (Table 1, no. 5) (Eq. 4) (8). Linking 2 with polychlorosilanes produces star-branched polymers (Table 1, no. 7) with up to 56 arms (9). Similar star-branched polymers with a dispersity of arms can be

made by addition of divinyl benzene to 2 (10).



A cyclic polymer (Table 1, no. 9) results when one treats a dilute solution of 4 with a coupling agent such as dibromo-p-xylene or dimethyldichlorosilane (11).

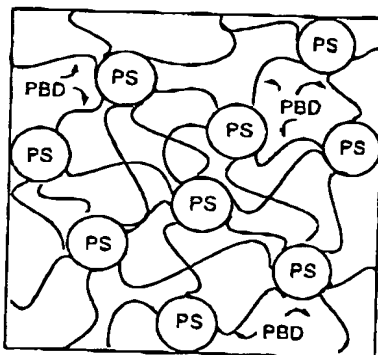
Butadiene and isoprene also give living polymers on initiation with 1 or 3. Considerable 1,2-polymerization results unless one uses alkyl lithium initiators in nonpolar solvents. Manufacture of styrene/butadiene/styrene block polymer, a thermoplastic elastomer, is at present the largest commercial use for living polymerizations. On cooling a polymer melt of this ABA block polymer, the hard styrene segments separate to form cross-links that are the basis for its rubberlike properties (Fig. 2).

Acrylate and methacrylate esters and amides plus acrylonitrile

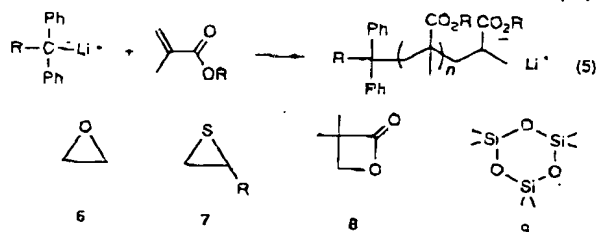
Table 1. Architectural forms of polymers available by living polymerization techniques.

Polymer	Application
1 Functional ended	Dispersing agents Synthesis of macromonomers
2 α,ω-difunctional	Elastomers synthesis Chain extension Cross-linking agents
3 AB Block	Dispersing agents Compatibilizers for polymer blending
4 ABA Block	Thermoplastic elastomers
5 Graft	Elastomers Adhesives
6 Comb	Elastomers Adhesives
7 Star	Rheology control Strengthening agents
8 Ladder	High-temperature plastics Membranes Elastomers
9 Cyclic	Rheology control
10 Amphiphilic network	Biocompatible polymers

2. Thermoplastic rubber from styrene butadiene block polymer (PS, polystyrene; PBD, polybutadiene).



represent a family of monomers called acrylics. Anionic living polymerization of acrylics presents several problems. Under the strongly basic conditions, initiators and anionic chain ends tend to attack the polar functional groups and α -protons. These side reactions kill living chain ends. If all of the chain ends are killed, polymerization stops. If only part of the chain ends are destroyed, the polymer molecular weight control will be lost and the molecular weight dispersity will rise. By working at -70°C or lower and initiating with a hindered initiator, for example, 1,1-diphenylhexyl lithium, one can prepare most of the architectural forms in Table 1 from methacrylates (Eq. 5; R is an alkyl group; Ph, phenyl) (12).



Acrylates do not polymerize well under comparable conditions. However, Teyssie *et al.* (13) showed that the addition of several equivalents of lithium chloride per chain end permits living polymerization at temperatures up to -20°C . In a more surprising result, Reetz and co-workers (14) have shown that a remarkable increase in chain and stability results by merely changing the counterion from lithium to tetrabutylammonium. Poly(butyl acrylate), $D = 1.14$, was produced at room temperature and above. Reetz speculates that side reactions such as ketene formation and end cyclization to form a cyclohexanone that eliminate the highly reactive tetrabutylammonium alkoxides are less likely to occur than those that eliminate lithium alkoxides.

At present, no commercial products are based on living polymerization of acrylics, although dispersing agents based on AB block polymers look promising.

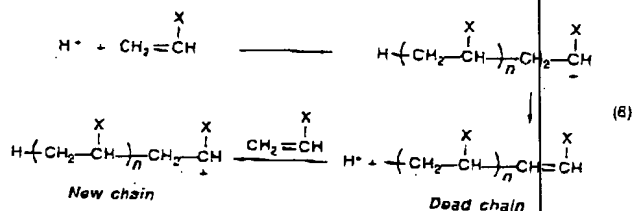
Ring-opening polymerization of strained heterocyclic compounds was one of the first types of living polymerization recognized (3). Sodium or potassium but not lithium alkoxides initiate ethylene oxide 6. These polymers are water-soluble and are used in non-ionic detergents. Double-ended polymers can be chain-extended with isocyanates to give elastomers and urethane foams. Propylene oxide and other substituted oxides do not give good living polymers by anionic initiation. However, substituted sulfides 7 as well as ethylene sulfide give living polymers when initiated with sulfide anion (15).

Strained lactones, for example, 8, form living polymers when initiated with tetraalkylammonium carboxylates (16). Ring cleavage occurs at the alkyl oxygen bond.

Living anionic polymerization of hexamethylcyclotrisiloxane, 9, a strained ring compound, results on initiation with lithium trimethylsilanoate (17). The more readily available octamethylcyclotetrasiloxane, an unstrained ring compound, does not give living polymer under similar conditions.

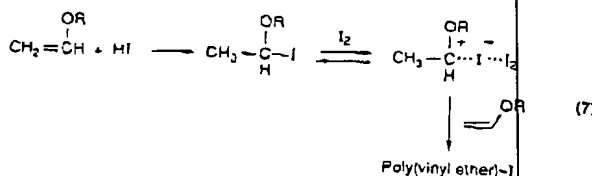
Cationic Living Polymerizations

Living cationic polymerization is more complex than its anionic counterpart. Carbenium ion chain ends generated by initiation of electron-rich monomers with strong protic acid readily transfer β -protons to start new chains (Eq. 6). The result is a lower



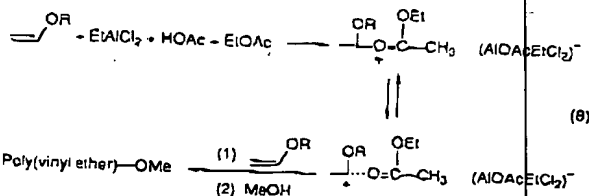
molecular weight than the theoretical value and many dead chain ends (18).

In 1984 Miyamoto, Sawamoto, and Higashimura reported a polymerization method for vinyl ethers that circumvented this problem (19). The chain ends were stored as a stable covalent iodoide. This iodide was activated by Lewis acid (electron-pair acceptor) catalysts to generate small amounts of active complexed carbenium ions. The activated ends insert monomer without chain transfer or termination (Eq. 7). The exact nature of these activated species is



still being debated. Higashimura's group has synthesized examples of most of the structures listed in Table 1 using the new procedure.

One disadvantage of the procedure is the light sensitivity of the iodo-ether end groups. In another breakthrough, Higashimura and co-workers (20) found a new way to stabilize the carbenium ion end groups. They used Lewis bases (electron-donor molecules) as additives. In this method, the carbenium-ion end groups are generated by the action of Lewis acid and a proton source on the monomer but are trapped by ethers or esters as onium salts (Eq. 8; Et, ethyl; Ac, acetyl). The exact nature of the end living group species needs to be



clarified further. To be effective, several equivalents of Lewis base are needed per equivalent of active end group. If dialkylsulfides are used as the donor molecules, the onium ion can be observed by nuclear magnetic resonance (NMR) (21). Kinetic studies show that donor molecules lower the rate of propagation, which indicates that monomer does not insert directly in the onium ion chain end.